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Gas Phase Reactions of the Ion $C_5H_5Fe^+$: A Kinetic Study

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The kinetics of gas phase reactions of the ion $C_5H_5Fe^+$ with oxygen (Me_2CO, Me_2O, MeOH, *iso*-propanol, H_2O) and nitrogen (NH_3, NH_2Me, $NHMe_2$, NMe_3) donor ligands have been studied by ion trap mass spectrometry. While in the literature reactions of the ion Fe^+, with the same ligands, the principal reaction path involves fragmentation in almost all the reactions of the ion $C_5H_5Fe^+$, formation of adduct ions is the major reaction path. The reactivity of these two ions is briefly compared in the ion trap conditions. Kinetic data for the ion $C_5H_5Fe^+$ indicate that the reactions show a large range of efficiency and a linear correlation is found between the log of the reaction rate constants and the ionization energy of ligands with the same donor atom. (J Am Soc Mass Spectrom 1998, 9, 314–319) © 1998 American Society for Mass Spectrometry

The study of gas phase ion–molecule reactions of metal ions has experienced a rapid growth in the last few years. Besides two recent reviews [1a, 1b], other papers reviewed various aspects of this topic [2–5]. Even if major attention has been devoted to the reaction pathways, data on the reaction rate constants for the ion–molecule reactions are now available for several systems. These last data show that most of the reactions occur with low efficiency as compared with the capture cross section. To our knowledge, there is no systematic study aimed to explore the effect of molecular parameters on the reaction efficiency in the early stage of the reaction; this aspect of metal ion reactivity is often ignored and in some cases different reasons for a low efficiency have been proposed. The exothermicity of the reaction seems to play an important role in reactions of Ti^+ [6] even if the literature data show some discrepancies [7]; the reaction of CoO^+ with methane was reported as an exothermic, thermal process with no significant activation energy and the low efficiency has been attributed to the presence of an activation barrier close to the energy of the entrance channel [8]. In any case the attention has been focused on the metal ion properties while the role of the entering ligand has not been explored.

To examine which kind of effects could be operative in reducing the efficiency of a gas phase reaction, few conditions are necessary; ligand exchange reactions or reactions with fragmentation of the entering ligand are not suitable since in these cases the reaction efficiency could be lowered by an energy barrier in a step following the first interaction between the ion and the neutral molecule so that only reactions which lead to the formation of stable adduct ions are to be considered. Reactions of $MC_5H_5^+$ ions were known as early as 1973, when several ion molecule reactions of $NiC_5H_5^+$ were studied [9]; many neutral stable adduct ions were observed suggesting that the presence of the ring is capable of stabilizing these kind of ions. Following this idea, and also taking into account the rather scarce information on the reactions of the ion $C_5H_5Fe^+$ with simple nonhydrocarbon molecules, we started to study its reactions with simple donor ligands. We found that formation of adduct ions is a frequent process in the reactions of $C_5H_5Fe^+$ so that it meets the condition for the study of reaction efficiency.

Experimental

Measurements have been done with a Finnigan ion trap mass spectrometer (ITMS). The general procedure to obtain kinetic data is as follows. Ferrocene is introduced in the ion trap via the direct insertion probe while helium and the ligand (L) are introduced in the mass spectrometer via two different standard gas inlet devices; the ferrocene pressure was usually around 8×10^{-5} Pa, the He pressure was kept at 3.5×10^{-2} Pa; the pressure of the ligands changed between about 7×10^{-6} and 3×10^{-4} Pa; the effective range for each ligand being determined by the reaction rate. The ion $C_5H_5Fe^+$ ($m/z = 121$) is formed by electron impact with an ionization time of 10 ms at a starting $m/z = 100$; in this way ions of lower mass are ejected from the ion source. The ion is then cooled for 50 ms and, after the isolation with the apex technique [10], several spectra are acquired at different reaction times. The scan function is

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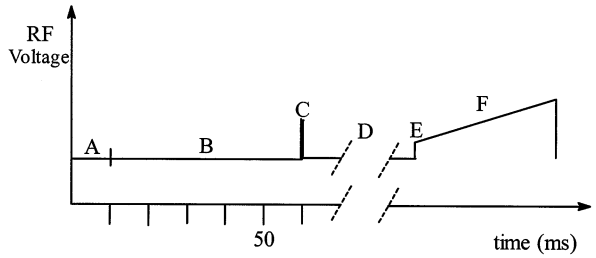


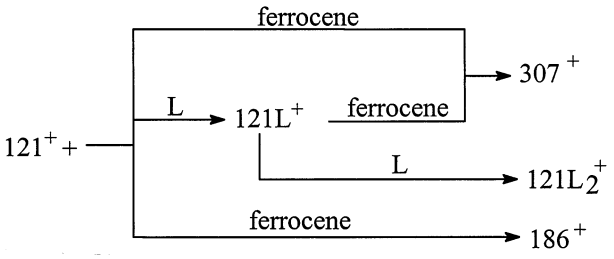
Figure 1. Scan function used to obtain the kinetic data: (**A**) ionization, (**B**) cool time, (**C**) isolation step, (**D**) reaction time, (**E**) settling scan start, (**F**) spectrum acquisition.

shown in Figure 1. The reaction time is changed by software; usually two spectra are collected at each reaction time for a total of 26–30 spectra in a time range sufficient to reduce the relative intensity of the ion $C_5H_5Fe^+$ from 100% to about 10%–5%. The relative intensity of this last ion was calculated with respect to the total ion intensities. In the adopted experimental conditions the ligand pressure, in a single kinetic run, is constant so that the disappearance of the ion $C_5H_5Fe^+$ must follow first order kinetics; from the plots of the ln of its relative intensity versus reaction time the pseudo first order rate constants can be obtained.

The gas pressure was monitored with a Bayard–Alpert gauge; the corrections for the different gauge sensitivity have been made by using literature ionization cross sections when available [11–13]; in absence of these data, as in the case of trimethyl- and dimethylamine, the ionization cross section has been estimated by using the relation between the polarizability and the cross section [12] and the postulate of atomic cross section additivity [14]; in this last case a fair agreement was found between the two calculated values. Kinetic data have been checked for homogeneity by using the F-test; reported uncertainties in Table 1 are the standard errors [15].

Results and Discussion

In the first measurements, which were made with a helium pressure of about 7×10^{-3} Pa and a cooling time of 5 ms, the semilog plots of the ion $C_5H_5Fe^+$ intensity versus reaction time did show a marked upward curvature. This behavior was ascribed to a nonhomogeneous distribution in energy of the ions formed by electron impact. It has been already suggested [16, 17], on the basis of the very high appearance potential of the ion $C_5H_5Fe^+$ from ferrocene, that this ion is formed with excess internal energy; following this suggestion we tried to thermalize the ions by increasing the cooling time (B, Figure 1) and the buffer gas pressure; after few attempts it was found that with a cooling time of 50 ms and a buffer gas pressure of 3.5×10^{-2} Pa the semilog plots became linear over the entire time interval.



Scheme I. Reaction sequence of the ion $C_5H_5Fe^+$ with gaseous ligands.

The Reactions of the Ion $C_5H_5Fe^+$

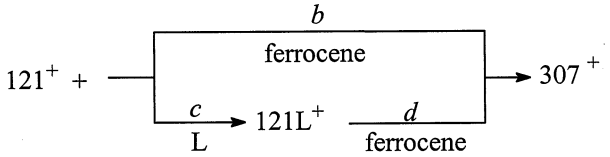
The reactions of the ion $C_5H_5Fe^+$ with oxygen containing ligands lead to the formation of the corresponding adduct ions, which will be indicated as $121L^+$. The ion $C_5H_5Fe^+$ also reacts with the neutral ferrocene [18, 19] with a charge exchange reaction to yield the ion at m/z 186, $(C_5H_5)_2Fe^+$, and with an addition reaction forming the ion at m/z 307, corresponding to $(C_5H_5)_3Fe_2^+$. It was also found that, at high L pressure, a double addition product ($121L_2^+$) is formed. The adduct ions $121L^+$ are also capable of reacting with the neutral ferrocene, giving rise to the ion at m/z 307.

This rather complex reaction scheme (Scheme 1) can be simplified with a proper choice of the experimental conditions; low pressure of the ferrocene in the ion source together with a high buffer gas pressure minimizing the charge exchange reaction [20], whereas the formation of the double adduct ion can be avoided by reducing the pressure range of L on the high pressure side. It was not possible to avoid the formation of the ion $(C_5H_5)_3Fe_2^+$. In the experimental conditions adopted in this work the important reactions are reported in Scheme 2.

A typical example of the spectra is reported in Figure 2 for the reaction of the monomethylamine at different reaction times; notice the presence of an ion at m/z 307 and the variation of the relative intensity of the ions at m/z 121 and 152.

The reaction of *iso*-propanol differs slightly from the above scheme; the adduct is accompanied by two other ions at m/z 139 and 163, with formulas $C_5H_5FeH_2O^+$ and $C_5H_5FeC_3H_6^+$, respectively. These ions must derive from the direct reaction of the ion $C_5H_5Fe^+$ with the neutral molecule because, after isolation, the adduct ion reacts only to form the ion $(C_5H_5)_3Fe_2^+$.

The reactions of the nitrogen containing ligands



Scheme II. Simplified reaction sequence of the ion $C_5H_5Fe^+$ with gaseous ligands.

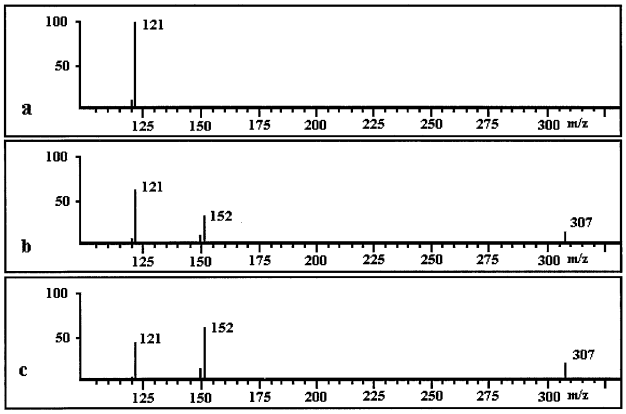


Figure 2. Mass spectra obtained in the reaction of the ion $C_5H_5Fe^+$ with NH_2CH_3 in the normal experimental conditions; reaction times: (**a**) 0, (**b**) 50, (**c**) 100 ms.

follow the above scheme for NH_3 and CH_3NH_2, whereas dimethylamine gives rise to a dehydrogenation product along with the adduct, and trimethylamine does not form the adduct ion but a dehydrogenation product (m/z = 178) and an ion at m/z 164 that should be formed by loss of a neutral CH_4 from the adduct ion.

A Comparison Between the Reactions of Fe^+ and $C_5H_5Fe^+$

There are significant differences between the reactions now observed with the ion $C_5H_5Fe^+$ and literature data concerning the reactions of Fe^+. The formation of stable adduct ions is not a frequently observed process for the oxygen containing ligands that form a variety of products ions; decarbonylation [21] is the principal reaction product of Fe^+ with acetone, whereas with dimethyl ether [21] the unique reaction product observed was $FeCH_2O^+$ (m/z = 86). According to a recent report [22], in the ion source of a mass spectrometer operating in chemical ionization conditions the formation of adduct ions is possible for methanol which, however, was reported [23] to form only the ion $FeOH^+$, but more recently [24] the formation of an adduct ion is found. Literature reactions of *iso*-propanol are more similar to those now observed since the formation of $Fe(C_3H_6)^+$ and $Fe(H_2O)^+$ has been found [23]. In the reactions between Fe^+ and methylamines the formation of adduct ions was not reported; the major reaction products are due to the loss, from the adduct ions, of H_2, CH_4, and FeH for mono-, di-, and trimethylamine, respectively [25].

Even if our primary interest is the study of reaction kinetics, it seemed worthwhile to ascertain if the different behavior of the two ions is because of a different reactivity or to the different experimental conditions. To this aim the reactions of Fe^+, obtained by electron impact from ferrocene, were briefly explored in the same experimental conditions adopted for the ion $C_5H_5Fe^+$. The results of this search are in partial agreement with the previous finding and are summarized as follows.

Acetone, at a pressure of 2.5×10^{-4} Pa, reacts with Fe^+ in the ITMS forming two ions at m/z 114 and 84 corresponding to $Fe[(CH_3)_2CO]^+$ and probably $Fe(CO)^+$; these two ions were observed with a reaction time of 50 ms; in these conditions their relative abundancies are equal and independent upon the cooling time applied after the formation of the Fe^+ ion and upon the He pressure.

Methanol, pressure 1.0×10^{-3} Pa, reacts with Fe^+ forming ions at m/z 88 ($FeCH_3OH^+$) and 118 ($FeC_2H_6O_2^+$); the relative abundance of this last ion decreases if the buffer gas pressure and/or the cooling time are lowered; a very weak signal is probably present at m/z 73 ($FeOH^+$). The structure of the ion at m/z = 88 should correspond to an adduct ion since its formation process is similar to that reported by Schroder et al. [24]. The reaction of dimethyl ether with Fe^+ gives rise to two principal ions at m/z 86 and 102; decreasing the cooling time of the ion Fe^+ and the He pressure, the adduct ion 102 disappears and there remains only the ion 86. Methylamine reacts with Fe^+ forming ions at m/z = 87 and 85, corresponding to the adduct and a dehydrogenation product, respectively; dimethylammine forms ions at m/z 101 and 85; once again, the presence of an adduct ion, even if of low intensity, is observed (m/z 101), whereas the most abundant ion at m/z 85 should be formed by the loss of CH_4 from the adduct ion [25]; the relative intensity of this last ion decreases if cooling time and the He pressure are increased. The most abundant ion observed in the reaction of trimethylammine with Fe^+ corresponds to the loss of neutral FeH from the adduct ion as already reported [25]. The above differences can be due to the different experimental conditions; the mentioned literature data have been taken with ICR and with pressure in the ion source well below those now adopted for the kinetic experiments; the fact that, in some cases, lowering the buffer gas pressure our results tend to match those of the literature, confirming this idea.

The structures of the adduct ions have been tested by collision induced dissociation; the ions were isolated and, after applying a tickle frequency for about 5 ms, are allowed to react for different time intervals up to about 50 ms; in every case the adduct ions break forming again an ion at m/z 121 as the sole product; this suggests that the ions we are dealing with are really the sum of the $C_5H_5Fe^+$ to the neutral molecule with no insertion reactions.

The above observations point to a different reactivity for the ion $C_5H_5Fe^+$ as compared to Fe^+; the insertion reactions that are responsible for the formation of the observed products in the reaction of Fe^+ are less pronounced. The observation of this kind of reactions in the case of *iso*-propanol indicates that they are still possible, ruling out the intervention of electronic or steric effects.

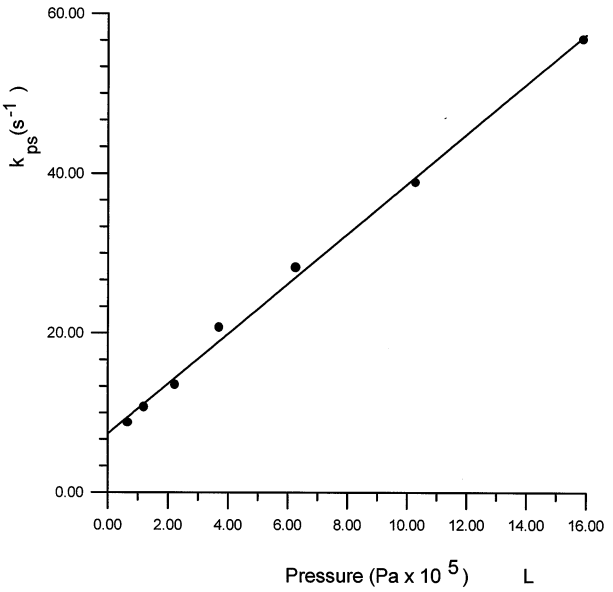


Figure 3. Pseudo first order rate constant for the reaction of $C_5H_5Fe^+$ with acetone vs. acetone pressure.

A thermodynamic factor should not be operative because, to make the reactions endothermic, a very strong decrease in the $(C_5H_5Fe–ligand)^+$ bond dissociation energy must be invoked; in the case of acetone, by using known thermodynamic data, it is possible to calculate that the decarbonylation reaction becomes endothermic if the $D(CpFe–CO)^+$ is lower than 22 kJ/mol, a result very unlikely in view of the fact that a similar decrease is not found in the bond dissociation energy for the products obtained in the reaction with *iso*-propanol. There remains only the possibility of a kinetic effect; the presence of the C_5H_5 ring could increase the energy of the adduct ions, whereas the activation energy for the insertion reactions remains about the same; in this way the energy of the transition state for the insertion reactions could become higher than that available to the system, reducing their occurrence; this same explanation was used for reactions of solvated gaseous ScO^+ [26]. According to this last argument the absence of a reaction path, which usually has been regarded as evidence for an endothermic reaction, could imply only a kinetic effect.

Kinetic Data

In the present experimental conditions the disappearance of the ion $C_5H_5Fe^+$ must follow first order kinetics as it was found in all cases so that a pseudo first order rate constant can be obtained from the semilog plot of the relative abundance of the ion $C_5H_5Fe^+$; according to the reactions depicted in Scheme 2, the disappearance of this ion is a consequence of two competitive reactions so that this pseudo first order constant is $k_{ps} = b[\text{ferrocene}]+c[\text{L}]$; because within a series of experiments the pressure of the ferrocene was constant and the pressure of L was changed, these pseudo first order constants should exhibit a linear dependence on the ligand pressure as it was always found. A typical plot is reported in Figure 3 for the reaction of acetone; these plots always have an intercept on the y axis, corresponding to the pseudo constant of the reaction of the ion $C_5H_5Fe^+$ with neutral ferrocene. From the slopes of these plots we get the experimental second order kinetic constants (k_1) reported in Table 1.

Table 1. Kinetic data for the reactions of the ion $C_5H_5Fe^+$

Molecule	k_1 *10^9	k_c*10^9	k_1/k_c
$(CH_3)_2CO$	1.89 ± 0.043	2.07	0.91
$(CH_3)_2O$	0.945 ± 0.016	1.31	0.72
$CH_3CH(OH)CH_3$	0.93 ± 0.044	1.47	0.63
CH_3OH	0.296 ± 0.0286	1.62	0.18
H_2O	0.023 ± 0.012	1.96	0.012
$(CH_3)_3$ N	0.765 ± 0.071	1.20	0.64
$(CH_3)_2$ NH	0.649 ± 0.038	1.29	0.50
CH_3NH_2	0.543 ± 0.016	1.48	0.37
NH_3	0.442 ± 0.020	1.81	0.24

In the same table we report the values of the collision rate constants (k_c) evaluated according to the method by Su and Chesnavich [27] along with the reactions efficiencies given by the ratio k_1/k_c. It is apparent that the reaction efficiency spans a large range, going from about 1 for the reaction of acetone to about 0.01 for the reaction of water. Such a large range requires some comment.

We must then focus the attention to the process forming the adducts ions. It is generally accepted [28] that the overall reaction between an ion and a neutral

$$A^+ + B \longrightarrow AB^+$$

can be analyzed in terms of the following mechanism:

$$A^+ + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [AB^+]^* \begin{cases} \xrightarrow{k_r} [AB^+] \\ \xrightarrow[k_c\beta M]{} [AB^+] \end{cases}$$

where k_1 is the bimolecular rate constant for the collisional complex formation; k_{-1} is the unimolecular redissociation rate constant; k_r is the unimolecular rate constant for the radiative stabilization reaction; k_c is the bimolecular rate constant for collisional stabilization of $[AB^+]^*$ by collision with neutral M; and β is the collisional stabilization efficiency. In our system M is the buffer gas He and the ligand L; the He pressure is always much greater then the L pressure (their ratio is usually greater then 100) so that, even if the efficiency of He in the collisional stabilization process is presumably lower then that of L [29], it seems possible to assume that the collision stabilization process is entirely because of He. From the above mechanism, by using the

steady state approximation on the intermediate $[AB^+]^*$, the rate of disappearance (ν) of the ion A^+ is

$$\nu = \frac{k_1 k_c \beta[He][B][A^+]}{k_{-1} + k_c\beta[He] + k_r} + \frac{k_r k_1 [A^+][B]}{k_{-1} + k_c\beta[He] + k_r}$$

Now, at high He pressure so that $k_c\beta[He] \gg k_{-1}+k_r$, the previous equation reduces to

$$\nu = k_1[A^+][B]$$

so that the observed second order rate constant is simply equal to k_1. There are two points to discuss which are crucial to the acceptance of this result: the first is the high assumed efficiency of the third body collision stabilization process and the second is the absence of an efficient radiative stabilization process. To test the first point we determined the rate constants for two ligands, i.e., methanol and *iso*-propanol, at higher He pressure; measurements made up to 1.3×10^{-2} Pa of the buffer gas did not show any significant variation of the rate constants so that it seems certain that in the adopted experimental conditions the saturation limit for the collision stabilization process is reached. There remains the possibility of a radiative stabilization; this process is known to be operative in absence of the third body process; however, the intercept on the y axis of the plots of Figure 3 could cast some doubt on this assumption. Since, for the reasons discussed above, it is not possible to collect kinetic data at low He pressure, we analyzed the intensity data by using the integrated rate equation [30] in such a way as to obtain all the rate constants for the kinetic Scheme 2. The equations employed were

$$[121] = e^{-at}$$

$$[121L] = c\left(\frac{1}{a-d}\,e^{-dt} + \frac{1}{d-a}\,e^{-at}\right)$$

$$[307] = \frac{b}{a}\,(1 - e^{-at}) + dc\left(\frac{1}{da} - \frac{1}{d(a-d)}\,e^{-dt} - \frac{1}{a(d-a)}\,e^{-at}\right)$$

where b, c, and d are the kinetic constants defined in Scheme 2 and $a = b+c$. A simple computer program, previously described [31], allowed us to obtain all the rate constants; good agreement was found by using these calculated values to reproduce the intensity data; a typical result is shown in Figure 4 for a kinetic run with acetone. The values of c obtained again give good linear plots versus the L pressure; application of the Student's criterion to these new values shows that, within a 95% interval confidence, they belong to the same universe of the values obtained by plotting the pseudo first order rate constants.

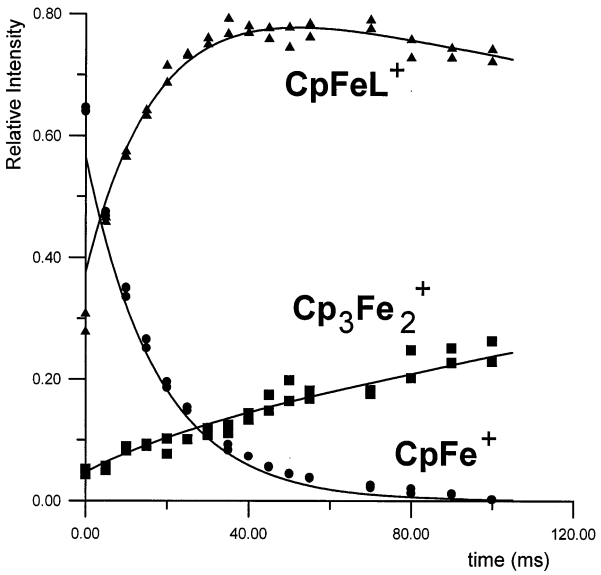


Figure 4. Experimental (dots) and calculated (solid lines) relative intensities of the ions in the reaction of $C_5H_5Fe^+$ with acetone.

These new plots, however, have much lower intercepts on the y axis and the estimated standard error on the intercept value suggests that the intercept could be really zero. Although we cannot be sure that a radiative stabilization process is not operative, it should not have great importance in this case. It seems therefore that the large range of reaction efficiency is not because of an experimental effect. We must admit that an energy barrier exists in the early step of the reactions and that the long range attractive forces are not sufficient to

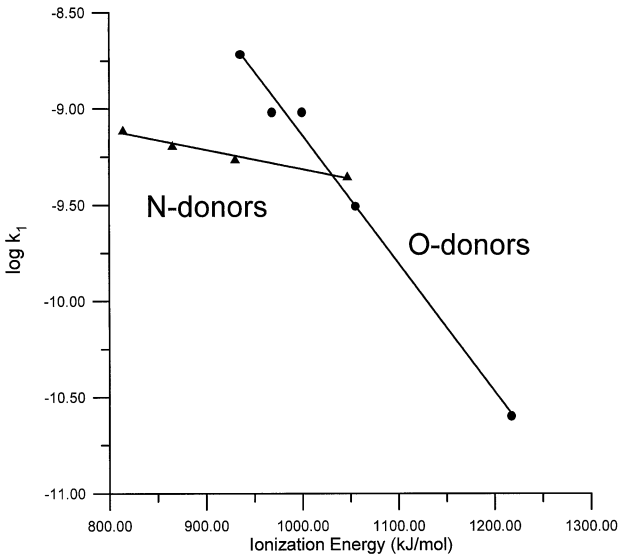


Figure 5. Rate constants vs. entering ligand ionization energies: (filled circle) oxygen containing ligands, (filled triangle) nitrogen containing ligands.

overcome this energy barrier. There are two consequence of some relevance that emerge from these results: caution must be exercised in using the collision capture cross section as the true value for k_1 and the ion–molecule interaction is not always so attractive in forming a specie with a minimum in the potential surface describing the reaction path. The rate constants reported above seem to depend on the ligand; a plot of the log k_1 versus the ionization energy of L gives two good linear correlations for ligands with the same donor atom; the plots are presented in Figure 5.

This behavior does not seem to be confined to the reactions under study; other similar correlations can be found by using literature data for the reactions of Mg^+ [32], Ag^+, and probably Cu^+ [33] with alcohols; work in progress in this laboratory indicates that also for the ion $C_5H_5Co^+$ the reaction efficiency changes with the nature of L. The meaning of these correlations is not yet clear but they indicate that as the energy of the ligand orbital, which should be responsible for the first interaction with the metal ion, decreases, the availability of this orbital for the reaction with a metal center decreases too. As a last comment, we wish to note that the reaction efficiency changes in the same probable order of the $C_5H_5Fe–L^+$ binding energy; this conclusion can also be reached in absence of the relevant data noting that in several metal ion systems [4, 34–37] the order of the $M–L^+$ binding energy is the same.

Acknowledgments

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